

Process for inscribing moldings

Description

- 5 The present invention relates to an improved process for inscribing thermoplastic polyesters by means of energy-rich radiation, to polyester molding compositions and to the inscribed moldings of any type.

- 10 Plastics can be inscribed by printing processes. In the last few years, however, laser inscription has become widely established. The advantages lie in the simply, rapidly and precisely performable, contactless (neither mechanical stress nor fouling of the workpiece), flexible (computer-controlled), clean and chemical-free processing. Laser units can be integrated without any problem into automatic production lines; finished plastic parts can be inscribed individually because a change in layout is possible in a
- 15 a simple and rapid manner with computer support. The inscription is effected without contact even at points which are difficult to access. Compared to conventional printing techniques, considerable advantages thus arise.

- The most important characterization parameter of the inscription achieved is the
- 20 legibility which can be quantified with the contrast. In addition to high contrast, sufficient depth of color and a very smooth surface are required. The inscription should be abrasion-resistant and chemical-resistant.

- To form a high-quality marking on a plastics molding, the absorption of laser light has
- 25 to bring about a color change reaction. Depending on wavelength, incident power, pulse length, etc., different interactions between laser light and plastic dominate in each case and a distinction is therefore drawn between a series of different laser-induced mechanisms which lead to lasting marking: thermochemical reaction, carbonization of the surface, melting, remelting, evaporation, sublimation, engraving, dyeing, foaming, photochemical reaction, ablation (material removal), bleaching-out of
- 30 dyes, removal of a coating layer.

- In the case of laser inscription, a distinction is drawn between two processes, mask (projection) inscription and beam deflection inscription (scanning of the laser beam). In
- 35 the case of mask inscription, pulsed lasers are used. A laser beam having sufficiently large aperture illuminates a mask which contains all of the information to be transferred. The mask is depicted using a lens on the surface to be inscribed; the information may be applied to the workpiece using a single laser pulse. In the case of large images, the mask may be scanned using several pulses. The maximum size of
- 40 the inscription field is restricted by the energy density required. The projection process thus allows rapid inscriptions; but since a mask has to be produced, it is not as flexible. In the case of beam deflection inscription, the laser beam is deflected onto the workpiece to be inscribed via two mobile mirrors and a planar field lens.

- The lasers used to date have been predominantly the CO₂ laser (wavelength 10.6 mm) and particularly the Nd:YAG laser (1.06 mm) or the frequency-doubled Nd:YAG laser (532 nm). However, the absorption coefficient of the plastics to be processed is often not high enough at these wavelengths to induce a color change in the polymeric material. Therefore, it is customary to add to the plastic in the course of its production suitable assistants and fillers which absorb strongly at the wavelength used and transfer the energy absorbed to the surrounding polymer matrix (for example addition of sensitizing dyes in the form of pigments, addition of toxic arsenic or Cd compounds, addition of suitable monomers in the copolymerization, coating of the substrate with special coating and dye films, inks, etc.). The incorporation of carbon black (DE-A 2936926) or animal charcoal (EP-A 522370) or of antimony trioxide into thermoplastic elastomers is known. Special plastics additives having high absorption capacity, especially for the wavelength of the Nd:YAG laser, enable markings with high contrast, good contour sharpness and good abrasion resistance (C. Herkt-Maetzky, Kunststoffe 81 (1991) 4). Further processes work with radiation-sensitive additives which can be bleached out (and possibly additional nondegradable compounds having lower radiation sensitivity). In that case, irradiation destroys the radiation-sensitive dyes and the background or complementary dye of the polymer matrix then remains at the irradiated sites resulting in a visually bright contrast marking. Such color changes lead to good contrasts (EP 327508). Plastics which contain commercial color pigments can be inscribed using the frequency-doubled Nd:YAG laser, since a large number of pigments and dyes absorb at 532 nm. The pigments are bleached out with the consequence of a color change. Addition of modified mica pigments allows molding compositions to be prepared which can be inscribed using the CO₂ laser (C. Herkt-Maetzky, Kunststoffe 81 (1991) 4). A process has also been described in which pigments are applied to a support material and are melted into the surface by a thermal route with the aid of a laser (EP-A 419 377).
- 30 DE-A 4133124 describes high molecular weight polymeric materials which have been inscribed with laser light and comprise inorganic transition group metal salts as an additive. EP-A 592942 discloses PA masses which comprise iron oxide pigments as fillers.
- 35 To improve the contrast in the inscription of polymers which have been colored black (white inscription on black background), the literature has described additives such as copper salts (for example US 5489639; EP-A 764683), titanium dioxide (EP-A 330689), tetrazoles (EP-A 572178 and EP-A 566312) or else antimony trioxide (EP-A 796743), for example. Also described have been additions of boron, zinc and tin salts
- 40 (WO 99/55773).

It is costly and inconvenient to modify plastics. The fillers added may adversely affect

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- the material properties of the plastic. Thus, additives for improving the inscribability may frequently have the consequence of unintended side effects such as reduced strength of the material or undesired colors when pigments are used. Therefore, special laser-sensitive additives have been sought which, incorporated into the plastic, do not affect other material performance properties. However, the sensitization is often only for one wavelength to which the system has been optimized.

- It was therefore an object of the present invention to provide a process for inscribing moldings based on thermoplastic polyesters which does not have the above-described disadvantages and enables the production of permanently high-contrast inscriptions in a manner which is technically simple to realize.

- According to the invention, this object is achieved by a process according to the preamble of claim 1, wherein the additive used for improving the inscribability is at least one highly branched or hyperbranched polycarbonate B1) having an OH number of from 1 to 600 mg KOH/g of polycarbonate (to DIN 53240, part 2), or at least one highly branched or hyperbranched polyester B2) of the A_xB_y type where x is at least 1.1 and y is at least 2.1, or mixtures thereof.

- The energy-rich radiation used in the process according to the invention generally has a wavelength in the range from 150 to 1500 nm, preferably in the range of 150-1100 nm.

- For example, mention should be made here of CO₂ lasers (10.6 μ m) and Nd:YAG lasers (1064 or 532 nm) or pulsed UV lasers, the latter in particular being excimer lasers having the following wavelengths:

	F ₂ excimer laser	157 nm
	ArF	193 nm
30	KrCl	222 nm
	KrF	248 nm
	XeCl	308 nm
	XeF	351 nm

- and also frequency-multiplied Nd:YAG lasers having wavelengths of 355 nm (frequency-tripled) or 266 nm (frequency-quadrupled).

- Particular preference is given to Nd:YAG lasers (1064 or 532 nm), KrF lasers (248 nm) and XeCl lasers (308 nm).

- The energy densities of the lasers used are generally in the range from 0.3 mJ/cm² to 50 J/cm², preferably from 0.5 mJ/cm² to 20 J/cm² and more preferably from 1 mJ/cm²

to 10 J/cm².

- When pulsed lasers are used, the pulse frequency is generally in the range from 0.1 to 10 000 Hz, preferably from 0.5 to 5000 Hz and in particular from 1 to 1000 Hz, and the
- 5 pulse lengths (duration of the individual pulses) is in the range from 0.1 to 1000 ns, preferably from 0.5 to 500 ns and more preferably from 1 to 100 ns.

- Depending on the energy density of the laser used, the pulse lengths and the type of molding irradiated, generally from 1 to 20 000, preferably from 1 to 5000 and in
- 10 particular from 1 to 3000 pulses are sufficient to achieve good inscriptions.

Appropriate lasers which may be used in the process according to the invention are commercially available.

- 15 Excimer lasers are particularly suitable for projection (mask process). However, it is also possible to conduct the beam using mobile mirrors (scanning). With homogeneous beam cross section, it is possible to irradiate a mask of about 2 cm x 2 cm. However, use of suitable optics allows the beam cross section also to be enlarged further.
- 20 Excimer lasers allow good inscription even with only one pulse (with appropriately matched energy density), so that very rapid inscriptions can also be produced in comparison to Nd:YAG lasers. In the mass production of injection moldings, for example, the inscription time has to be less than the injection molding time (< approx. 30 s) divided by the number of mold cavities. It follows that the injection
- 25 moldings in these cases have to be inscribed at high speeds. Such high speeds are not always possible using the Nd:YAG laser, and are only achievable using 1-pulse mask bombardment.

- Even higher demands are made on the inscription speed by continuous processes, for
- 30 example profile extrusion with material speeds of several m/s. For this purpose, even high inscription speeds of Nd:YAG lasers are no longer sufficient.

Useful radiation sources are also continuous UV lamps such as Hg, Xe or deuterium lamps. Such products are also commercially available.

- 35 In the process according to the invention, moldings based on thermoplastic polyesters A) or mixtures of these polyesters with up to 70% by weight, based on the total weight of the components and further additives C), are inscribed by means of energy-rich radiation.

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As component (A), the inventive molding compositions comprise from 10 to 99.9% by weight, preferably from 30 to 99.5% by weight and in particular from 30 to 99.3% by weight, of at least one thermoplastic polymer which is different from B).

- 5 In general, polyesters A) based on aromatic dicarboxylic acids and an aliphatic or aromatic dihydroxyl compound are used.

A first group of preferred polyesters is that of polyalkylene terephthalates, in particular those having from 2 to 10 carbon atoms in the alcohol moiety.

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Such polyalkylene terephthalates are known per se and are described in the literature. Their main chain comprises an aromatic ring which stems from the aromatic dicarboxylic acid. The aromatic ring may also be substituted, for example by halogen, such as chlorine or bromine, or by C₁-C₄-alkyl groups such as methyl, ethyl, iso- or n-propyl, or n-, iso- or tert-butyl groups.

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These polyalkylene terephthalates may be prepared by reacting aromatic dicarboxylic acids, their esters or other ester-forming derivatives with aliphatic dihydroxyl compounds in a manner known per se.

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Preferred dicarboxylic acids include 2,6-naphthalenedicarboxylic acid, terephthalic acid and isophthalic acid, or mixtures thereof. Up to 30 mol%, preferably not more than 10 mol%, of the aromatic dicarboxylic acids may be replaced by aliphatic or cycloaliphatic dicarboxylic acids, such as adipic acid, azelaic acid, sebacic acid, dodecanedioic acids and cyclohexanedicarboxylic acids.

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Of the aliphatic dihydroxyl compounds, preference is given to diols having from 2 to 6 carbon atoms, in particular 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,4-hexanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol and neopentyl glycol, or mixtures thereof.

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Particularly preferred polyesters (A) include polyalkylene terephthalates which derive from alkanediols having from 2 to 6 carbon atoms. Of these, preference is given in particular to polyethylene terephthalate, polypropylene terephthalate and polybutylene terephthalate, or mixtures thereof. Preference is further given to PET and/or PBT which comprise, as further monomer units, up to 1% by weight, preferably up to 0.75% by weight, of 1,6-hexanediol and/or 2-methyl-1,5-pentanediol.

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The viscosity number of the polyesters (A) is generally in the range from 50 to 220, preferably from 80 to 160 (measured in a 0.5% by weight solution in a phenol/o-dichlorobenzene mixture in a weight ratio of 1:1 at 25°C) to ISO 1628.

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Preference is given in particular to polyesters whose carboxyl end group content is up to 100 meq/kg of polyester, preferably up to 50 meq/kg of polyester and in particular up to 40 meq/kg of polyester. Such polyesters may be prepared, for example, by the process of DE-A 44 01 055. The carboxyl end group content is typically determined by titration
5 methods (e.g. potentiometry).

Especially preferred molding compositions comprise, as component A), a mixture of polyesters other than PBT, for example polyethylene terephthalate (PET). The proportion of the polyethylene terephthalate, for example, in the mixture is preferably
10 up to 50% by weight, in particular from 10 to 35% by weight, based on 100% by weight of A).

It is also advantageous to use PET recyclates (also known as scrap PET), if appropriate in a mixture with polyalkylene terephthalates such as PBT.

15 Recyclates are generally:

- 1) those known as post-industrial recyclates: these are production wastes in polycondensation or in processing, for example sprues from injection molding,
20 start-up material from injection molding or extrusion, or edge trims from extruded sheets or films.
- 2) post-consumer recyclates: these are plastic items which are collected and processed after utilization by the end consumer. In terms of volume, blow-molded
25 PET bottles for mineral water, soft drinks and juices are easily the predominant items.

Both types of recycle may be used either as ground material or in the form of granules. In the latter case, the crude recyclates, after being separated and purified,
30 are melted and granulated using an extruder. This usually eases the handling and the free flow and the metering for further processing steps.

The recyclates used may either be granulated or in the form of ground material. The edge length should not be more than 10 mm, preferably less than 8 mm.

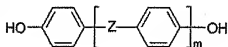
35 Owing to the hydrolytic cleavage of polyesters in the course of processing (as a result of traces of moisture), it is advisable to predry the recycle. The residual moisture content after drying is preferably < 0.2%, in particular < 0.05%.

40 Another group to be mentioned is that of fully aromatic polyesters which derive from aromatic dicarboxylic acids and aromatic dihydroxyl compounds.

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- Suitable aromatic dicarboxylic acids are the compounds already mentioned for the polyalkylene terephthalates. Preference is given to using mixtures of from 5 to 100 mol% of isophthalic acid and from 0 to 95 mol% of terephthalic acid, in particular mixtures of about 80% terephthalic acid with 20% isophthalic acid up to about equivalent amounts of these two acids.

The aromatic dihydroxyl compounds preferably have the general formula



- in which Z is an alkylene or cycloalkylene group having up to 8 carbon atoms, an arylene group having up to 12 carbon atoms, a carbonyl group, a sulfonyl group, an oxygen or sulfur atom, or a chemical bond, and in which m is from 0 to 2. The compounds may also bear C₁-C₆-alkyl or alkoxy groups and fluorine, chlorine or bromine as substituents on the phenylene groups.

Examples of parent compounds for these compounds are

- dihydroxybiphenyl,
di(hydroxyphenyl)alkane,
di(hydroxyphenyl)cycloalkane,
di(hydroxyphenyl) sulfide,
di(hydroxyphenyl) ether,
di(hydroxyphenyl) ketone,
di(hydroxyphenyl) sulfoxide,
 α,α' -di(hydroxyphenyl)dialkylbenzene,
di(hydroxyphenyl) sulfone, di(hydroxybenzoyl)benzene,
resorcinol, and
hydroquinone, and also their ring-alkylated and ring-halogenated derivatives.

Of these, preference is given to

- 4,4'-dihydroxybiphenyl,
2,4-di(4'-hydroxyphenyl)-2-methylbutane,
 α,α' -di(4-hydroxyphenyl)-p-diisopropylbenzene,
2,2-di(3'-methyl-4'-hydroxyphenyl)propane, and
2,2-di(3'-chloro-4'-hydroxyphenyl)propane,

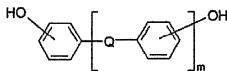
and in particular to

- 2,2-di(4'-hydroxyphenyl)propane
2,2-di(3',5'-dichlorodihydroxyphenyl)propane,
5 1,1-di(4'-hydroxyphenyl)cyclohexane,
3,4'-dihydroxybenzophenone,
4,4'-dihydroxydiphenyl sulfone and
2,2-di(3',5'-dimethyl-4'-hydroxyphenyl)propane
10 or mixtures thereof.

It is of course also possible to use mixtures of polyalkylene terephthalates and fully aromatic polyesters. These generally comprise from 20 to 98% by weight of the polyalkylene terephthalate and from 2 to 80% by weight of the fully aromatic polyester.

- 15 It is of course also possible to use polyester block copolymers, such as copolyether-esters. Such products are known per se and are described in the literature, for example in US-A 3 651 014. Corresponding products are also available commercially, for example Hytrel® (DuPont).

- 20 According to the invention, polyesters also include halogen-free polycarbonates. Examples of suitable halogen-free polycarbonates are those based on diphenols of the general formula



- 25 in which Q is a single bond, a C₁-C₆-alkylene, a C₂-C₃-alkylidene, a C₃-C₆-cycloalkylidene group, a C₆-C₁₂-arylene group, or else -O-, -S- or -SO₂-, and m is an integer from 0 to 2.

- 30 The diphenols may also have substituents on the phenylene radicals, such as C₁-C₆-alkyl or C₁-C₆-alkoxy.

- 35 Examples of preferred diphenols of the formula are hydroquinone, resorcinol, 4,4'-dihydroxybiphenyl, 2,2-bis(4-hydroxyphenyl)propane, 2,4-bis(4-hydroxyphenyl)-2-methylbutane and 1,1-bis(4-hydroxyphenyl)cyclohexane. Particular preference is given to 2,2-bis(4-hydroxyphenyl)propane and 1,1-bis(4-hydroxyphenyl)cyclohexane, and also to 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.

Either homopolycarbonates or copolycarbonates are suitable as component A, and preference is given to the copolycarbonates of bisphenol A, as well as to bisphenol A homopolymer.

- 5 The suitable polycarbonates may be branched in a known manner, preferably by incorporating 0.05 to 2.0 mol%, based on the sum of the diphenols used, of at least trifunctional compounds, for example those having three or more phenolic OH groups.

- 10 Particularly suitable polycarbonates have been found to be those which have relative viscosities η_{rel} of from 1.10 to 1.50, in particular from 1.25 to 1.40. This corresponds to average molecular weights M_w (weight-average) of from 10 000 to 200 000 g/mol, preferably from 20 000 to 80 000 g/mol.

- 15 The diphenols of the general formula are known per se or can be prepared by known processes.

- The polycarbonates can be prepared, for example, by reacting the diphenols with phosgene in the interfacial process, or with phosgene in the homogeneous-phase process (known as the pyridine process), and in each case the desired molecular weight is achieved in a known manner by means of an appropriate amount of known chain terminators. (In relation to polydiorganosiloxane-comprising polycarbonates see, for example, DE-A 33 34 782.)

- 25 Examples of suitable chain terminators are phenol, p-tert-butylphenol, or else long-chain alkylphenols such as 4-(1,3-tetramethylbutyl)phenol as in DE-A 28 42 005, or monoalkylphenols, or dialkylphenols with a total of from 8 to 20 carbon atoms in the alkyl substituents as in DE-A 35 06 472, such as p-nonylphenyl, 3,5-di-tert-butylphenol, p-tert-octylphenol, p-dodecylphenol, 2-(3,5-dimethylheptyl)phenol and 4-(3,5-dimethylheptyl)phenol.

- 30 In the context of the present invention, halogen-free polycarbonates are polycarbonates made from halogen-free diphenols, halogen-free chain terminators and, if appropriate, halogen-free branching agents. The content of subordinate amounts at the ppm level of hydrolyzable chlorine, resulting, for example, from the preparation of the polycarbonates with phosgene in the interfacial process, is not regarded as meriting the term halogen-containing in the context of the invention. Such polycarbonates with contents of hydrolyzable chlorine at the ppm level are halogen-free polycarbonates in the context of the present invention.

- 40 Further suitable components A) include amorphous polyester carbonates, for which phosgene has been replaced by aromatic dicarboxylic acid units such as isophthalic acid and/or terephthalic acid units in the preparation. For further details, reference may

be made at this point to EP-A 711 810.

Further suitable copolycarbonates having cycloalkyl radicals as monomer units are described in EP-A 365 916.

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It is also possible for bisphenol A to be replaced by bisphenol TMC. Such polycarbonates are obtainable from Bayer with the trademark APEC HT®.

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As component B) for improving the inscribability, the inventive molding compositions comprise from 0.01 to 10% by weight, preferably from 0.1 to 9% by weight and in particular from 0.1 to 5% by weight, of an alkaline earth metal carbonate, alkali metal carbonate, alkaline earth metal sulfate or alkali metal sulfate, or mixtures thereof.

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Useful alkali metals and alkaline earth metals include all elements of main groups I and II, preference being given to Ca, Mg and Ba.

Suitable sulfates include anions such as SO_4^{2-} , SO_3^{2-} , HSO_3^- , HSO_4^- , $\text{S}_2\text{O}_7^{2-}$, preference being given to sulfates und carbonates.

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Corresponding preferred salts are BaSO_4 , CaCO_3 and MgCO_3 , and also mixed salts such as $\text{CaMg}(\text{CO}_3)_2$ (black chalk).

BaSO_4 compounds are commercially available as Blanc Fixe F, white barite, lithopone (ZnS/BaSO_4 mixture) from Sachtleben.

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As component C), the polyester molding compositions may comprise up to 70% by weight, preferably up to 50% by weight, of further additives.

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In particular, the inventive molding compositions may comprise from 0.01 to 50% by weight, preferably from 0.5 to 20% by weight and in particular from 0.7 to 10% by weight, of C1) at least one highly branched or hyperbranched polycarbonate having an OH number of from 1 to 600 mg KOH/g of polycarbonate, preferably from 10 to 550 mg KOH/g of polycarbonate and in particular from 50 to 550 mg KOH/g of polycarbonate (to DIN 53240, part 2), or of at least one hyperbranched polyester as component C2) or mixtures thereof as described below.

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In the context of this invention, hyperbranched polycarbonates C1) are uncrosslinked macromolecules having hydroxyl groups and carbonate groups which have both structural and molecular non-uniformity. One possible structure is based on a central molecule in the same way as dendrimers, but with non-uniform chain length of the branches. Another possibility is a linear structure with functional pendant groups, or else a combination of the two extremes, with linear and branched molecular portions.

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See also P.J. Flory, J. Am. Chem. Soc. 1952, 74, 2718, and H. Frey et al., Chem. Eur. J. 2000, 6, No. 14, 2499 for the definition of dendrimeric and hyperbranched polymers.

5 "Hyperbranched" in the context of the present invention means that the degree of branching (DB), i.e. the average number of dendritic linkages plus the average number of end groups per molecule, is from 10 to 99.9%, preferably from 20 to 99%, more preferably 20 - 95%.

10 "Dendrimeric" in the context of the present invention means that the degree of branching is from 99.9 to 100%. See H. Frey et al., Acta Polym. 1997, 48, 30 for the definition of "degree of branching" and is defined as

$$\text{DB} = \frac{\text{T} + \text{Z}}{\text{T} + \text{Z} + \text{L}} \times 100\%,$$

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(where T is the average number of terminal monomer units, Z the average number of branched monomer units and L the average number of linear monomer units in the macromolecules of the particular substances).

20 Component B1) preferably has a number-average molecular weight M_n of from 100 to 15 000 g/mol, preferably from 200 to 12 000 g/mol and in particular from 500 to 10 000 g/mol (GPC, PMMA standard).

25 The glass transition temperature T_g is in particular from -80°C to $+140^\circ\text{C}$, preferably from -60 to 120°C (by DSC, DIN 53765).

In particular, the viscosity (mPas) at 23°C (to DIN 53019) is from 50 to 200 000, in particular from 100 to 150 000 and most preferably from 200 to 100 000.

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Component C1) is preferably obtainable by a process which comprises at least the following steps:

a) reaction of at least one organic carbonate (A) of the general formula
35 $\text{RO}[(\text{CO})_n\text{OR}]$ with at least one aliphatic, araliphatic or aromatic alcohol (B) which has at least 3 OH groups with elimination of alcohols ROH to give one or more condensation products (K), where R is in each case independently a straight-chain or branched, aliphatic, araliphatic or aromatic hydrocarbon radical having from 1 to 20 carbon atoms, and where the R radicals may also be joined together
40 to form a ring and n is an integer from 1 to 5, or

ab) reaction of phosgene, diphosgene or triphosgene with the abovementioned

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alcohol (B) with hydrogen chloride elimination

and

- 5 b) intermolecular reaction of the condensation products (K) to give a highly functional highly branched or highly functional hyperbranched polycarbonate,

the quantitative ratio of the OH groups to the carbonates in the reaction mixture being selected in such a way that the condensation products (K) have an average either of
10 one carbonate group and more than one OH group or one OH group and more than one carbonate group.

The starting material used may be phosgene, diphosgene or triphosgene, and preference is given to organic carbonates.

- 15 Each of the R radicals of the organic carbonates (A) used as a starting material and having the general formula $RO(CO)_nOR$ is independently a straight-chain or branched aliphatic, araliphatic, or aromatic hydrocarbon radical having from 1 to 20 carbon atoms. The two R radicals may also be joined together to form a ring. The radical is
20 preferably an aliphatic hydrocarbon radical and more preferably a straight-chain or branched alkyl radical having from 1 to 5 carbon atoms, or a substituted or unsubstituted phenyl radical.

- In particular, simple carbonates of the formula $RO(CO)_nOR$ are used; n is preferably
25 from 1 to 3, in particular 1.

- Dialkyl or diaryl carbonates may be prepared, for example, from the reaction of aliphatic, araliphatic or aromatic alcohols, preferably monoalcohols, with phosgene. They may also be prepared via oxidative carbonylation of the alcohols or phenols by
30 means of CO in the presence of noble metals, oxygen, or NO_x . In relation to preparation methods for diaryl or dialkyl carbonates, see also "Ullmann's Encyclopedia of Industrial Chemistry", 6th edition, 2000 Electronic Release, Verlag Wiley-VCH.

- Examples of suitable carbonates comprise aliphatic, araliphatic or aromatic carbonates,
35 such as ethylene carbonate, propylene 1,2- or 1,3-carbonate, diphenyl carbonate, ditolyl carbonate, dixylyl carbonate, dinaphthyl carbonate, ethyl phenyl carbonate, dibenzyl carbonate, dimethyl carbonate, diethyl carbonate, dipropyl carbonate, dibutyl carbonate, diisobutyl carbonate, dipentyl carbonate, dihexyl carbonate, dicyclohexyl carbonate, diheptyl carbonate, dioctyl carbonate, didecyl carbonate, or didodecyl
40 carbonate.

Examples of carbonates in which n is greater than 1 comprise dialkyl dicarbonates

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such as di(tert-butyl) dicarbonate, or dialkyl tricarbonates such as di(tert-butyl) tr carbonate.

- Preference is given to using aliphatic carbonates, in particular those in which the radicals comprise from 1 to 5 carbon atoms, for example dimethyl carbonate, diethyl carbonate, dipropyl carbonate, dibutyl carbonate or diisobutyl carbonate.

The organic carbonates are reacted with at least one aliphatic alcohol (B) which has at least 3 OH groups, or mixtures of two or more different alcohols.

- Examples of compounds having at least three OH groups comprise glycerol, trimethylolmethane, trimethylolethane, trimethylolpropane, 1,2,4-butanetriol, tris(hydroxymethyl)amine, tris(hydroxyethyl)amine, tris(hydroxypropyl)amine, pentaerythritol, diglycerol, triglycerol, polyglycerols, bis(trimethylolpropane), tris(hydroxymethyl) isocyanurate, tris(hydroxyethyl) isocyanurate, phloroglucinol, trihydroxyltoluene, trihydroxydimethylbenzene, phloroglucides, hexahydrobenzene, 1,3,5-benzenetriethanol, 1,1,1-tris(4'-hydroxyphenyl)methane, 1,1,1-tris(4'-hydroxyphenyl)ethane, bis(trimethylolpropane), or sugars, for example glucose, trihydric or higher polyhydric polyetherols based on trihydric or higher polyhydric alcohols and ethylene oxide, propylene oxide, or butylene oxide, or polyesterols. Particular preference is given to glycerol, trimethylolethane, trimethylolpropane, 1,2,4-butanetriol, pentaerythritol, and also their polyetherols based on ethylene oxide or propylene oxide.

- These polyhydric alcohols may also be used in a mixture with dihydric alcohols (B'), with the proviso that the average total OH functionality of all of the alcohols used is greater than 2. Examples of suitable compounds having two OH groups comprise ethylene glycol, diethylene glycol, triethylene glycol, 1,2- and 1,3-propanediol, dipropylene glycol, tripropylene glycol, neopentyl glycol, 1,2-, 1,3- and 1,4-butanediol, 1,2-, 1,3- and 1,5-pentanediol, hexanediol, cyclopentanediol, cyclohexanediol, cyclohexanedimethanol, bis(4-hydroxycyclohexyl)methane, bis(4-hydroxycyclohexyl)ethane, 2,2-bis(4-hydroxycyclohexyl)propane, 1,1'-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane, resorcinol, hydroquinone, 4,4'-dihydroxyphenyl, bis(4-bis-(hydroxyphenyl) sulfide, bis(4-hydroxyphenyl) sulfone, bis(hydroxymethyl)benzene, bis(hydroxymethyl)toluene, bis(p-hydroxyphenyl)methane, bis(p-hydroxyphenyl)ethane, 2,2-bis(p-hydroxyphenyl)propane, 1,1-bis(p-hydroxyphenyl)cyclohexane, dihydroxybenzophenone, dihydric polyether polyols based on ethylene oxide, propylene oxide, butylene oxide, or mixtures of these, polytetrahydrofuran, polycaprolactone, or polyesterols based on diols and dicarboxylic acids.

- The diols serve for fine adjustment of the properties of the polycarbonate. If dihydric alcohols are used, the ratio of dihydric alcohols (B') to the at least trihydric alcohols (B)

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is set by the person skilled in the art as a function of the desired properties of the polycarbonate. The amount of the alcohol(s) (B') is generally from 0 to 50 mol%, based on the total amount of all alcohols (B) and (B'). The amount is preferably from 0 to 45 mol%, more preferably from 0 to 35 mol%, and most preferably from 0 to 30 mol%.

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The reaction of phosgene, diphosgene, or triphosgene with the alcohol or alcohol mixture generally takes place with elimination of hydrogen chloride, and the reaction of the carbonates with the alcohol or alcohol mixture to give the inventive highly functional highly branched polycarbonate takes place with elimination of the monohydric alcohol or phenol from the carbonate molecule.

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After the reaction, i.e. with no further modification, the highly functional highly branched polycarbonates formed by the process according to the invention are terminated by hydroxyl groups and/or by carbonate groups. They have good solubility in various solvents, for example in water, alcohols, such as methanol, ethanol, butanol, alcohol/water mixtures, acetone, 2-butanone, ethyl acetate, butyl acetate, methoxypropyl acetate, methoxyethyl acetate, tetrahydrofuran, dimethylformamide, dimethylacetamide, N-methylpyrrolidone, ethylene carbonate or propylene carbonate.

15

In the context of this invention, a highly functional polycarbonate is a product which, in addition to the carbonate groups which form the polymer skeleton, further has at least three, preferably at least six, more preferably at least ten, terminal or pendant functional groups. The functional groups are carbonate groups and/or OH groups. There is in principle no upper restriction on the number of terminal or pendant functional groups, but products having a very high number of functional groups can have undesired properties, such as high viscosity or poor solubility. The highly functional polycarbonates of the present invention usually have not more than 500 terminal or pendant functional groups, preferably not more than 100 terminal or pendant functional groups.

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30

In the preparation of the highly functional polycarbonates C1), it is necessary to adjust the ratio of the compounds comprising OH groups to phosgene or carbonate in such a way that the simplest resulting condensation product (hereinafter termed condensation product (K)) comprises an average of either one carbonate group or carbamoyl group and more than one OH group or one OH group and more than one carbonate group or carbamoyl group. The simplest structure of the condensation product (K) composed of a carbonate (A) and a di- or polyalcohol (B) gives rise to the XY_n or Y_nX arrangement where X is a carbonate group, Y is a hydroxyl group, and n is generally a number from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3. The reactive group which is the single resulting group is generally referred to as "focal group" below.

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For example, when the reaction ratio in the preparation of the simplest condensation

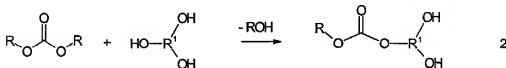
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product (K) from a carbonate and a dihydric alcohol is 1:1, the average result is a molecule of XY type, illustrated by the general formula 1.



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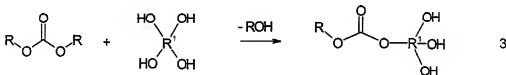
In the preparation of the condensation product (K) from a carbonate and a trihydric alcohol with a reaction ratio of 1:1, the average result is a molecule of XY₂ type, illustrated by the general formula 2. The focal group here is a carbonate group.



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In the preparation of the condensation product (K) from a carbonate and a tetrahydric alcohol, likewise with the reaction ratio 1:1, the average result is a molecule of XY₃ type, illustrated by the general formula 3. The focal group here is a carbonate group.

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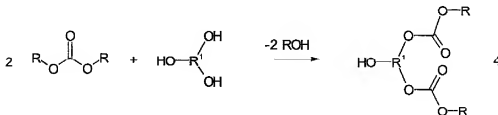


In the formulae 1-3, R is as defined at the outset and R¹ is an aliphatic or aromatic radical.

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The condensation product (K) can also be prepared, for example, from a carbonate and a trihydric alcohol, illustrated by the general formula 4, the molar reaction ratio being 2:1. Here, the average result is a molecule of X₂Y type; the focal group here is an OH group. In the formula 4, R and R¹ are each as defined in the formulae 1-3.

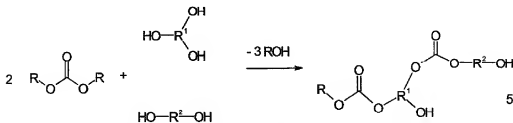
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When difunctional compounds, for example a dicarbonate or a diol, are additionally added to the components, this brings about an extension of the chains, as illustrated in

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the general formula 5, for example. The average result is again a molecule of XY_2 type; the focal group is a carbonate group.



- 5 In formula 5, R^2 is an organic, preferably aliphatic radical; R and R' are each as defined above.

- It is also possible to use two or more condensation products (K) for the synthesis. It is possible in this context firstly to use a plurality of alcohols or a plurality of carbonates. It is also possible to obtain mixtures of various condensation products of different structure by virtue of the selection of the ratio of the alcohols used and of the carbonates or of the phosgenes. This will be explained using the example of the reaction of a carbonate with a trihydric alcohol. If the starting materials are introduced in a ratio of 1:1, as illustrated in (II), the result is an XY_2 molecule. When the starting materials are used in a ratio of 2:1, as illustrated in (IV), an X_2Y molecule is obtained. At a ratio between 1:1 and 2:1, a mixture of XY_2 and X_2Y molecules is obtained.

- According to the invention, the simple condensation products (K) described by way of example in the formulae 1-5 preferentially react intermolecularly to form highly functional polycondensation products, hereinafter referred to as polycondensation products (P). The reaction to give the condensation product (K) and to give the polycondensation product (P) usually takes place at a temperature of from 0 to 250°C, preferably from 60 to 160°C, in bulk or in solution. It is generally possible to use all solvents which are inert toward the particular reactants. Preference is given to using organic solvents, for example decane, dodecane, benzene, toluene, chlorobenzene, xylene, dimethylformamide, dimethylacetamide or Solvent Naphtha.

- In a preferred embodiment, the condensation reaction is carried out in bulk. The phenol or the monohydric alcohol ROH released in the reaction can be removed by distillation from the reaction equilibrium to accelerate the reaction, if appropriate under reduced pressure.

- If removal by distillation is intended, it is regularly advisable to use those carbonates which liberate alcohols ROH having a boiling point below 140°C in the reaction.

- To accelerate the reaction, it is also possible to add catalysts or catalyst mixtures. Suitable catalysts are compounds which catalyze esterification or transesterification

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- reactions, for example alkali metal hydroxides, alkali metal carbonates, alkali metal hydrogencarbonates, preferably of sodium, of potassium or of cesium, tertiary amines, guanidines, ammonium compounds, phosphonium compounds, organoaluminum, organotin, organozinc, organotitanium, organozirconium or organobismuth compounds, or else what are known as double metal cyanide (DMC) catalysts, as described, for example, in DE 10138216 or DE 10147712.

- Preference is given to using potassium hydroxide, potassium carbonate, potassium hydrogencarbonate, diazabicyclooctane (DABCO), diazabicyclononene (DBN), diazabicycloundecene (DBU), imidazoles such as imidazole, 1-methylimidazole or 1,2-dimethylimidazole, titanium tetrabutoxide, titanium tetraisopropoxide, dibutyltin oxide, dibutyltin dilaurate, tin dioctoate, zirconium acetylacetonate or mixtures thereof.

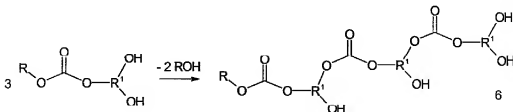
- The catalyst is generally added in an amount of from 50 to 10 000 ppm by weight, preferably from 100 to 5000 ppm by weight, based on the amount of the alcohol mixture or alcohol used.

- It is also possible to control the intermolecular polycondensation reaction by addition of the suitable catalyst or else by selection of a suitable temperature. It is also possible to adjust the average molecular weight of the polymer (P) via the composition of the starting components and via the residence time.

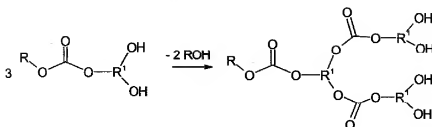
- The condensation products (K) and the polycondensation products (P) prepared at elevated temperature are typically stable at room temperature for a prolonged period.

- The nature of the condensation products (K) makes it possible for the condensation reaction to result in polycondensation products (P) with different structures, which have branching but no crosslinking. Moreover, in the ideal case, the polycondensation products (P) have either one carbonate group as focal group and more than two OH groups or else one OH group as focal group and more than two carbonate groups. The number of the reactive groups depends on the nature of the condensation products (K) used and the degree of polycondensation.

- For example, a condensation product (K) of the general formula 2 can react by triple intermolecular condensation to give two different polycondensation products (P) which are represented in the general formulae 6 and 7:



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In formulae 6 and 7, R and R¹ are each as defined above.

For the termination of the intermolecular polycondensation reaction, there are various methods. For example, the temperature can be lowered to a range in which the reaction stops and the product (K) or the polycondensation product (P) is storage-stable.

It is also possible to deactivate the catalyst, for example by addition of Lewis acids or protic acids in the case of basic catalysts.

In another embodiment, as soon as a polycondensation product (P) with the desired degree of polycondensation is present as a result of the intermolecular reaction of the condensation product (K), a product having groups reactive toward the focal group of (P) may be added to the product (P) to terminate the reaction. For example, in the case of a carbonate group as focal group, a mono-, di-, or polyamine may be added. In the case of a hydroxyl group as focal group, for example, a mono-, di- or polyisocyanate, a compound comprising epoxy groups or an acid derivative which reacts with OH groups can be added to the product (P).

The inventive highly functional polycarbonates are usually prepared in a pressure range from 0.1 mbar to 20 bar, preferably at from 1 mbar to 5 bar, in reactors or reactor batteries which are operated batchwise, semicontinuously or continuously.

By virtue of the abovementioned adjustment of the reaction conditions and, if appropriate, by virtue of the selection of the suitable solvent, the inventive products can be further processed without further purification after their preparation.

In a further preferred embodiment, the product is stripped, i.e. freed of low molecular weight, volatile compounds. To this end, once the desired degree of conversion has been attained, the catalyst may optionally be deactivated and the low molecular weight, volatile constituents, for example monoalcohols, phenols, carbonates, hydrogen chloride or highly volatile oligomeric or cyclic compounds, can be removed by distillation, if appropriate with introduction of a gas, preferably nitrogen, carbon dioxide

or air, if appropriate at reduced pressure.

In a further preferred embodiment, the inventive polycarbonates may obtain other functional groups in addition to the functional groups already present as a result of the reaction. The functionalization may take place during the molecular weight buildup, or
5 else subsequently, i.e. after completion of the actual polycondensation.

When, prior to or during the molecular weight buildup, components are added which have further functional groups or functional elements in addition to hydroxyl or
10 carbonate groups, a polycarbonate polymer with randomly distributed functionalities other than the carbonate or hydroxyl groups is obtained.

These effects can, for example, be achieved by addition, during the polycondensation, of compounds which bear further functional groups or functional elements, such as
15 mercapto groups, primary, secondary or tertiary amino groups, ether groups, derivatives of carboxylic acids, derivatives of sulfonic acids, derivatives of phosphonic acids, silane groups, siloxane groups, aryl radicals or long-chain alkyl radicals. In addition to hydroxyl groups, carbonate groups or carbamoyl groups. For modification by means of carbamate groups, it is possible, for example, to use ethanolamine,
20 propanolamine, isopropanolamine, 2-(butylamino)ethanol, 2-(cyclohexylamino)ethanol, 2-amino-1-butanol, 2-(2'-aminoethoxy)ethanol or higher alkoxylation products of ammonia, 4-hydroxypiperidine, 1-hydroxyethylpiperazine, diethanolamine, dipropanolamine, diisopropanolamine, tris(hydroxymethyl)aminomethane, tris(hydroxyethyl)-aminomethane, ethylenediamine, propylenediamine, hexamethylenediamine or
25 isophoronediamine.

For modification with mercapto groups, it is possible, for example, to use mercapto-ethanol. By way of example, tertiary amino groups can be produced via incorporation of N-methyldiethanolamine, N-methyldipropanolamine or N,N-dimethylethanolamine.
30 Ether groups can be obtained, for example, by cocondensation of dihydric or higher polyhydric polyetherols. Reaction with long-chain alkanediols can introduce long-chain alkyl radicals; reaction with alkyl or aryl diisocyanates generates polycarbonates having alkyl, aryl, and urethane groups or urea groups.

35 Addition of dicarboxylic acids or tricarboxylic acids, for example dimethyl terephthalate or tricarboxylic esters, allows ester groups to be obtained.

Subsequent functionalization can be obtained by reacting the resulting highly functional highly branched or highly functional hyperbranched polycarbonate in an additional
40 process step (step c)) with a suitable functionalizing reagent which can react with the OH and/or carbonate groups or carbamoyl groups of the polycarbonate.

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Highly functional highly branched or highly functional hyperbranched polycarbonates comprising hydroxyl groups can be modified, for example, by addition of molecules comprising acid groups or isocyanate groups. For example, polycarbonates comprising acid groups can be obtained by reaction with compounds comprising anhydride groups.

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Moreover, highly functional polycarbonates comprising hydroxyl groups can also be converted to highly functional polycarbonate polyether polyols by reaction with alkylene oxides, for example ethylene oxide, propylene oxide, or butylene oxide.

- 10 A great advantage of the process lies in its economic viability. Both the reaction to give a condensation product (K) or polycondensation product (P) and the reaction of (K) or (P) to give polycarbonates with other functional groups or elements can take place in one reaction apparatus, which is technically and economically advantageous.

- 15 As component C2), the inventive mixtures may comprise at least one hyperbranched polyester of A_xB_y type where

x is at least 1.1, preferably at least 1.3, in particular at least 2

y is at least 2.1, preferably at least 2.5, in particular at least 3.

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It is of course also possible to use mixtures as units A and/or B.

An A_xB_y -type polyester is a condensate composed of an x-functional molecule A and a y-functional molecule B. An example is a polyester composed of adipic acid as

- 25 molecule A (x = 2) and glycerol as molecule B (y = 3).

In the context of this invention, hyperbranched polyesters C2) are uncrosslinked macromolecules having hydroxyl groups and carboxyl groups which have both structural and molecular non-uniformity. One possible structure is based on a central molecule in the same way as dendrimers, but with non-uniform chain length of the branches. Another possibility is a linear structure with functional pendant groups, or else a combination of the two extremes, with linear and branched molecular portions. See also P.J. Flory, J. Am. Chem. Soc. 1952, 74, 2718, and H. Frey et al., Chem. Eur. J. 2000, 6, No. 14, 2499 for the definition of dendrimeric and hyperbranched polymers.

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"Hyperbranched" in the context of the present invention means that the degree of branching (DB), i.e. the average number of dendritic linkages plus the average number of end groups per molecule, is from 10 to 99.9%, preferably from 20 to 99%, more preferably from 20 to 95%.

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"Dendrimeric" in the context of the present invention means that the degree of branching is from 99.9 to 100%. See H. Frey et al., Acta Polym. 1997, 48, 30 for the

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definition of "degree of branching".

- Component C2) preferably has an M_n of from 300 to 30 000 g/mol, in particular from 400 to 25 000 g/mol and very particularly from 500 to 20 000 g/mol, determined by means of GPC, PMMA standard, dimethylacetamide eluent.

- C2) preferably has an OH number of from 0 to 600 mg KOH/g of polyester, preferably of from 1 to 500 mg KOH/g of polyester, in particular from 20 to 500 mg KOH/g of polyester, to DIN 53240, and preferably a COOH number of from 0 to 600 mg KOH/g of polyester, preferably from 1 to 500 mg KOH/g of polyester, and in particular from 2 to 500 mg KOH/g of polyester.

- The T_g is preferably from -50°C to 140°C , and in particular from -50 to 100°C (by means of DSC, to DIN 53765).

- Preference is given in particular to those components B2) in which at least one OH or COOH number is greater than 0, preferably greater than 0.1 and in particular greater than 0.5.

- The inventive component C2) is in particular obtainable via the processes described below, specifically by reacting

- (a) one or more dicarboxylic acids or one or more derivatives thereof with one or more at least trihydric alcohols,

or

- (b) one or more tricarboxylic acids or higher polycarboxylic acids or one or more derivatives thereof with one or more diols

- in the presence of a solvent and optionally in the presence of an inorganic, organometallic or low molecular weight organic catalyst, or of an enzyme. The reaction in solvent is the preferred preparation method.

- In the context of the present invention, highly functional hyperbranched polyesters C2) have molecular and structural non-uniformity. Their molecular non-uniformity distinguishes them from dendrimers, and they can therefore be prepared at considerably lower cost.

- The dicarboxylic acids which can be reacted according to variant (a) include, for example, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, undecane- α,ω -dicarboxylic acid, dodecane-

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α,ω -dicarboxylic acid, cis- and trans-cyclohexane-1,2-dicarboxylic acid, cis- and trans-cyclohexane-1,3-dicarboxylic acid, cis- and trans-cyclohexane-1,4-dicarboxylic acid, cis- and trans-cyclopentane-1,2-dicarboxylic acid, and cis- and trans-cyclopentane-1,3-dicarboxylic acid,

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and the abovementioned dicarboxylic acids may be substituted by one or more radicals selected from

C₁-C₁₀-alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, isoamyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, n-octyl, 2-ethylhexyl, n-nonyl and n-decyl,

C₃-C₁₂-cycloalkyl groups such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, and cyclododecyl; preference is given to cyclopentyl, cyclohexyl and cycloheptyl;

alkylene groups such as methylene or ethylidene, or

C₆-C₁₄-aryl groups such as phenyl, 1-naphthyl, 2-naphthyl, 1-anthryl, 2-anthryl, 9-anthryl, 1-phenanthryl, 2-phenanthryl, 3-phenanthryl, 4-phenanthryl, and 9-phenanthryl, preferably phenyl, 1-naphthyl and 2-naphthyl, more preferably phenyl.

Examples of representatives of substituted dicarboxylic acids include: 2-methylmalonic acid, 2-ethylmalonic acid, 2-phenylmalonic acid, 2-methylsuccinic acid, 2-ethylsuccinic acid, 2-phenylsuccinic acid, itaconic acid, 3,3-dimethylglutaric acid.

The dicarboxylic acids which can be reacted according to variant (a) also include ethylenically unsaturated acids, for example maleic acid and fumaric acid, and aromatic dicarboxylic acids such as phthalic acid, isophthalic acid or terephthalic acid.

It is also possible to use mixtures of two or more of the abovementioned representatives.

The dicarboxylic acids may either be used as such or in the form of derivatives.

Derivatives are preferably

- the relevant anhydrides in monomeric or else polymeric form,
- mono- or dialkyl esters, preferably mono- or dimethyl esters, or the corresponding mono- or diethyl esters, or else the mono- and dialkyl esters

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derived from higher alcohols such as n-propanol, isopropanol, n-butanol, isobutanol, tert-butanol, n-pentanol, n-hexanol,

- and also mono- and divinyl esters, and

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- mixed esters, preferably methyl ethyl esters.

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In the context of the preferred preparation, it is also possible to use a mixture of a dicarboxylic acid and one or more of its derivatives. Equally, it is possible to use a mixture of a plurality of different derivatives of one or more dicarboxylic acids.

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Particularly preference is given to using succinic acid, glutaric acid, adipic acid, phthalic acid, isophthalic acid, terephthalic acid, or their mono- or dimethyl esters. Very particular preference is given to using adipic acid.

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Examples of at least trihydric alcohols which can be reacted are: glycerol, butane-1,2,4-triol, n-pentane-1,2,5-triol, n-pentane-1,3,5-triol, n-hexane-1,2,6-triol, n-hexane-1,2,5-triol, n-hexane-1,3,6-triol, trimethylolbutane, trimethylolpropane or ditrimethylolpropane, trimethylethanol, pentaerythritol or dipentaerythritol; sugar alcohols such as mesoerythritol, threitol, sorbitol, mannitol, or mixtures of the above at least trihydric alcohols. Preference is given to using glycerol, trimethylolpropane, trimethylethanol and pentaerythritol.

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Examples of tricarboxylic acids or polycarboxylic acids which can be reacted according to variant (b) are benzene-1,2,4-tricarboxylic acid, benzene-1,3,5-tricarboxylic acid, benzene-1,2,4,5-tetracarboxylic acid and mellitic acid.

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Tricarboxylic acids or polycarboxylic acids can be used in the inventive reaction either as such or in the form of derivatives.

Derivatives are preferably

- the relevant anhydrides in monomeric or else polymeric form,

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- mono-, di- or trialkyl esters, preferably mono-, di- or trimethyl esters, or the corresponding mono-, di- or triethyl esters, or else the mono-, di- and triesters derived from higher alcohols such as n-propanol, isopropanol, n-butanol, isobutanol, tert-butanol, n-pentanol, n-hexanol, or else mono-, di- or trivinyl esters

40

- and mixed methyl ethyl esters.

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In the context of the present invention, it is also possible to use a mixture of a tri- or polycarboxylic acid and one or more of its derivatives. In the context of the present invention it is equally possible to use a mixture of a plurality of different derivatives of one or more tri- or polycarboxylic acids in order to obtain component C2).

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Examples of diols used for variant (b) of the present invention are ethylene glycol, propane-1,2-diol, propane-1,3-diol, butane-1,2-diol, butane-1,3-diol, butane-1,4-diol, butane-2,3-diol, pentane-1,2-diol, pentane-1,3-diol, pentane-1,4-diol, pentane-1,5-diol, pentane-2,3-diol, pentane-2,4-diol, hexane-1,2-diol, hexane-1,3-diol, hexane-1,4-diol, 10 hexane-1,5-diol, hexane-1,6-diol, hexane-2,5-diol, heptane-1,2-diol, 1,7-heptanediol, 1,8-octanediol, 1,2-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,2-decanediol, 1,12-dodecanediol, 1,2-dodecanediol, 1,5-hexadiene-3,4-diol, cyclopentanediols, cyclohexanediols, inositol and derivatives, 2-methylpentane-2,4-diol, 2,4-dimethylpentane-2,4-diol, 2-ethylhexane-1,3-diol, 2,5-dimethylhexane-2,5-diol, 2,2,4-trimethylpentane-1,3-diol, pinacol, diethylene glycol, triethylene glycol, dipropylene glycol, 15 tripropylene glycol, polyethylene glycols $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ or polypropylene glycols $\text{HO}[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}]_n\text{H}$ or mixtures of two or more representative compounds of the above compounds, where n is an integer and $n = 4 - 25$. One hydroxyl group or else both hydroxyl groups in the aforementioned diols may also be replaced by SH groups. 20 Preference is given to ethylene glycol, propane-1,2-diol, and diethylene glycol, triethylene glycol, dipropylene glycol, and tripropylene glycol.

The molar ratio of the molecules A to molecules B in the A_xB_y polyester in the variants (a) and (b) is from 4:1 to 1:4, in particular from 2:1 to 1:2.

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The at least trihydric alcohols reacted according to variant (a) of the process may have hydroxyl groups each of the same reactivity. Preference is also given here to at least trihydric alcohols whose OH groups initially have the same reactivity, but where reaction with at least one acid group can induce a decline in reactivity of the remaining 30 OH groups caused by steric or electronic effects. For example, this is the case when trimethylolpropane or pentaerythritol is used.

However, the at least trihydric alcohols reacted according to variant (a) may also have hydroxyl groups having at least two different chemical reactivities.

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The different reactivity of the functional groups may either stem from chemical causes (e.g. primary/secondary/tertiary OH group) or from steric causes.

For example, the triol may be a triol which has primary and secondary hydroxyl groups; 40 the preferred example is glycerol.

When the inventive reaction is carried out according to variant (a), preference is given

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to working in the absence of diols and monohydric alcohols.

When the inventive reaction is carried out according to variant (b), preference is given to working in the absence of mono- or dicarboxylic acids.

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The process according to the invention is carried out in the presence of a solvent. Examples of suitable solvents are hydrocarbons such as paraffins or aromatics. Particularly suitable paraffins are n-heptane and cyclohexane. Particularly suitable aromatics are toluene, ortho-xylene, meta-xylene, para-xylene, xylene in the form of an isomer mixture, ethylbenzene, chlorobenzene and ortho- and meta-dichlorobenzene. Other very particularly suitable solvents in the absence of acidic catalysts are: ethers, for example dioxane or tetrahydrofuran, and ketones, for example methyl ethyl ketone and methyl isobutyl ketone.

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- 15 According to the invention, the amount of solvent added is at least 0.1% by weight, based on the mass of the starting materials used and to be reacted, preferably at least 1% by weight and more preferably at least 10% by weight. It is also possible to use excesses of solvent, based on the mass of starting materials used and to be reacted, for example from 1.01 to 10 times the amount. Solvent amounts of more than
- 20 100 times the mass of the starting materials used and to be reacted are not advantageous, because the reaction rate declines markedly at markedly lower concentrations of the reactants, which leads to uneconomically long reaction times.

- To carry out the process preferred in accordance with the invention, it is possible to work in the presence of a dehydrating agent as an additive, which is added at the start of the reaction. Suitable examples are molecular sieves, in particular 4 Å molecular sieve, MgSO_4 and Na_2SO_4 . During the reaction, it is also possible to add further dehydrating agent or to replace dehydrating agent with fresh dehydrating agent. During the reaction, it is also possible to distill off the water or alcohol formed and, for example,
- 30 to use a water separator.

The process can be carried out in the absence of acidic catalysts. Preference is given to working in the presence of an acidic inorganic, organometallic or organic catalyst, or mixtures of two or more acidic inorganic, organometallic or organic catalysts.

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- In the context of the present invention, examples of acidic inorganic catalysts are sulfuric acid, phosphoric acid, phosphonic acid, hypophosphorous acid, aluminum sulfate hydrate, alum, acidic silica gel (pH = 6, in particular = 5) and acidic aluminum oxide. Further examples of compounds which can be used as acidic inorganic catalysts are aluminum compounds of the general formula $\text{Al}(\text{OR})_3$ and titanates of the general formula $\text{Ti}(\text{OR})_4$, where each of the R radicals may be the same or different and is selected independently from
- 40

C₁-C₁₀-alkyl radicals, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl, sec-pentyl, neopentyl, 1,2-dimethylpropyl, isoamyl, n-hexyl, isohexyl, sec-hexyl, n-heptyl, isoheptyl, n-octyl, 2-ethylhexyl, n-nonyl and
5 n-decyl,

C₃-C₁₂-cycloalkyl radicals, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, and cyclododecyl;
10 preference is given to cyclopentyl, cyclohexyl and cycloheptyl.

Each of the R radicals in Al(OR)₃ or Ti(OR)₄ is preferably the same and selected from isopropyl or 2-ethylhexyl.

Examples of preferred acidic organometallic catalysts are selected from dialkyltin
15 oxides R₂SnO where R is as defined above. A particularly preferred representative compound of acidic organometallic catalysts is di-n-butyltin oxide, which is commercially available as "oxo-tin", or di-n-butyltin dilaurate.

Preferred acidic organic catalysts are acidic organic compounds having, for example,
20 phosphate groups, sulfonic acid groups, sulfate groups or phosphonic acid groups. Particular preference is given to sulfonic acids, for example para-toluenesulfonic acid. The acidic organic catalysts used can also be acidic ion exchangers, for example sulfonic acid group-containing polystyrene resins which are crosslinked with about 2 mol% of divinylbenzene.

25 It is also possible to use combinations of two or more of the abovementioned catalysts. It is also possible to use an immobilized form of those organic or organometallic, or else inorganic catalysts which take the form of discrete molecules.

30 If the intention is to use acidic inorganic, organometallic or organic catalysts, the amount used in accordance with the invention is from 0.1 to 10% by weight, preferably from 0.2 to 2% by weight, of catalyst.

The process according to the invention is carried out under an inert gas atmosphere,
35 i.e., for example, under carbon dioxide, nitrogen or a noble gas, among which particular mention should be made of argon.

The process according to the invention is carried out at temperatures of from 60 to 200°C. Preference is given to working at temperatures of from 130 to 180°C, in
40 particular up to 150°C or lower. Particular preference is given to maximum temperatures up to 145°C, very particular preference to temperatures up to 135°C.

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- The pressure conditions of the process according to the invention are not critical per se. It is possible to work at distinctly reduced pressure, for example at from 10 to 500 mbar. The process according to the invention may also be carried out at pressures above 500 mbar. For reasons of simplicity, preference is given to the reaction at atmospheric pressure; however, it is also possible to work at slightly increased pressure, for example up to 1200 mbar. It is also possible to work at distinctly elevated pressure, for example at pressures up to 10 bar. Preference is given to the reaction at atmospheric pressure.
- 10 The reaction time for the process according to the invention is typically from 10 minutes to 25 hours, preferably from 30 minutes to 10 hours and more preferably from one to 8 hours.
- Once the reaction has ended, the highly functional hyperbranched polyesters can easily be isolated, for example by filtering off the catalyst and concentrating, the concentration typically being effected at reduced pressure. Further very suitable workup methods are precipitation after addition of water, followed by washing and drying.
- 20 Component C2) can also be prepared in the presence of enzymes or decomposition products of enzymes (according to DE-A 101 63163). In the context of the present invention, the dicarboxylic acids reacted in accordance with the invention are not included in the acidic organic catalysts.
- 25 Preference is given to using lipases or esterases. Very suitable lipases and esterases are *Candida cylindracea*, *Candida lipolytica*, *Candida rugosa*, *Candida antarctica*, *Candida utilis*, *Chromobacterium viscosum*, *Geotrichum viscosum*, *Geotrichum candidum*, *Mucor javanicus*, *Mucor mihei*, pig pancreas, *Pseudomonas* spp., *Pseudomonas fluorescens*, *Pseudomonas cepacia*, *Rhizopus arrhizus*, *Rhizopus delemar*, *Rhizopus niveus*, *Rhizopus oryzae*, *Aspergillus niger*, *Penicillium roquefortii*, *Penicillium camembertii*, or esterase from *Bacillus* spp. and *Bacillus thermoglucosidasius*. Particular preference is given to *Candida antarctica* lipase B. The enzymes listed are commercially available, for example from Novozymes Biotech Inc., Denmark.
- 35 The enzyme is preferably used in immobilized form, for example on silica gel or Lewatit®. The processes for immobilizing enzymes are known per se, for example from Kurt Faber, "Biotransformations in organic chemistry", 3rd edition 1997, Springer Verlag, Chapter 3.2 "Immobilization" pp. 345-356. Immobilized enzymes are commercially available, for example from Novozymes Biotech Inc., Denmark.
- 40

The amount of immobilized enzyme used is from 0.1 to 20% by weight, in particular

from 10 to 15% by weight, based on the mass of all of the starting materials used and to be reacted.

- The process according to the invention is carried out at temperatures above 60°C.
- 5 Preference is given to working at temperatures of 100°C or lower. Preference is given to temperatures up to 80°C, very particular preference is given to temperatures of from 62 to 75°C, and even greater preference is given to temperatures of from 65 to 75°C.

- The process according to the invention is carried out in the presence of a solvent.
- 10 Examples of suitable solvents are hydrocarbons such as paraffins or aromatics. Particularly suitable paraffins are n-heptane and cyclohexane. Particularly suitable aromatics are toluene, ortho-xylene, meta-xylene, para-xylene, xylene in the form of an isomer mixture, ethylbenzene, chlorobenzene and ortho- and meta-dichlorobenzene. Further very particularly suitable solvents are: ethers, for example dioxane or
- 15 tetrahydrofuran, and ketones, for example methyl ethyl ketone and methyl isobutyl ketone.

- The amount of solvent added is at least 5 parts by weight, based on the mass of the starting materials used and to be reacted, preferably at least 50 parts by weight and
- 20 more preferably at least 100 parts by weight. Amounts of more than 10 000 parts by weight of solvent are undesirable, because the reaction rate declines markedly at markedly lower concentrations, which leads to uneconomically long reaction times.

- The process according to the invention is carried out at pressures above 500 mbar.
- 25 Preference is given to the reaction at atmospheric pressure or slightly elevated pressure, for example up to 1200 mbar. It is also possible to work under distinctly elevated pressure, for example at pressures up to 10 bar. Preference is given to the reaction at atmospheric pressure.
- 30 The reaction time of the process according to the invention is typically from 4 hours to 6 days, preferably from 5 hours to 5 days and more preferably from 8 hours to 4 days.

- Once the reaction has ended, the highly functional hyperbranched polyesters can be isolated, e.g. by filtering off the enzyme and concentrating the mixture, the
- 35 concentration typically being carried out at reduced pressure. Other very suitable workup methods are precipitation after addition of water, followed by washing and drying.

- The highly functional hyperbranched polyesters obtainable by the process according to the invention feature particularly low contents of discolored and resinified material. For
- 40 the definition of hyperbranched polymers, see also: P.J. Flory, J. Am. Chem. Soc. 1952, 74, 2718, and A. Sunder et al., Chem. Eur. J. 2000, 6, no. 1, 1-8. However, in the

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- context of the present invention, "highly functional hyperbranched" means that the degree of branching, i.e. the average number of dendritic linkages plus the average number of end groups per molecule, is from 10 to 99.9%, preferably from 20 to 99%, more preferably from 30 to 90% (on this subject, see H. Frey et al. *Acta Polym.* 1997, 48, 30).

- The inventive polyesters have a molecular weight M_w of from 500 to 50 000 g/mol, preferably from 1000 to 20 000 g/mol, more preferably from 1000 to 19 000 g/mol. The polydispersity is from 1.2 to 50, preferably from 1.4 to 40, more preferably from 1.5 to 30 and most preferably from 1.5 to 10. They are typically very soluble, i.e. clear solutions can be prepared using up to 50% by weight, in some cases even up to 80% by weight, of the inventive polyesters in tetrahydrofuran (THF), n-butyl acetate, ethanol, and numerous other solvents, with no gel particles detectable by the naked eye.

- The inventive highly functional hyperbranched polyesters are carboxyl-terminated, carboxyl- and hydroxyl-terminated, and preferably hydroxyl-terminated.

- The ratios of the components C1) to C2) are preferably from 1:20 to 20:1, in particular from 1:15 to 15:1, and very particularly from 1:5 to 5:1.

- As component C), the inventive molding compositions may comprise from 0 to 70% by weight, in particular up to 50% by weight, of further additives which are different from B).

- Examples include fibrous or particulate fillers such as glass fibers or mineral fillers such as wollastonite, elastomeric polymers (for example EP and EPDM rubbers, TPUs, core-shell polymers), UV stabilizers, nucleating agents, flame retardants, in particular nitrogen-containing flame retardants such as melamine cyanurate or phosphorus-containing flame retardants such as calcium phosphinate, plasticizers, oxidation retardants and heat stabilizers.

- In a preferred embodiment of the process according to the invention, an additive (better inscription contrast) used in addition is an inorganic transition group metal salt in amounts of from 0 to 10% by weight, preferably from 0.01 to 10% by weight, preferably from 0.005 to 5% by weight, preferentially from 0.01 to 2% by weight and in particular from 0.02 to 1% by weight. A transition group metal is generally understood to mean elements which have d electrons in their outer electron shell (d^1 – d^{10}).

- Among the inorganic transition group metal salts, particularly suitable transition group metal salts have been found to be those in which the transition group metal has a d^8 to d^{10} , preferably d^9 , electron configuration, i.e. Cu, Ag, Au, in particular Cu and Ag. Further preferred inorganic transition group metal salts are the halides, pseudohalides

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and sulfates. The pseudohalides include linear anions such as cyanide, fulminate, cyanate, thiocyanate and azide, and nonlinear anions such as dicyanamide, dicyanophosphide, tricyanomethanide and nitrosodicyanomethanide. Particular preference is given to the chlorides, bromides, thiocyanates and sulfates, and also ZnO
5 and ZnS.

In addition to transition metal salts if appropriate, further additives which are typically used to inscribe moldings with lasers are also used; however, the addition of further additives is not required.

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The inventive thermoplastic molding compositions may be prepared by processes known per se, by mixing the starting components in customary mixing devices such as screw extruders, Brabender mills or Banbury mills and subsequent extrusion. After the extrusion, the extrudate can be cooled and comminuted. It is also possible to premix
15 individual components and then to add the remaining starting materials individually or likewise mixed. The mixing temperatures are generally from 230 to 290°C.

In a further preferred operating mode, the components B) and, if appropriate, C) can be mixed with a polyester prepolymer, formulated and granulated. The resulting granule,
20 in the solid phase, is subsequently condensed up to the desired viscosity under inert gas, continuously or batchwise, at a temperature below the melting point of component A).

The inventive thermoplastic molding compositions feature good inscribability and
25 flowability with simultaneously good mechanical properties.

In particular, the processing of the individual components (without clumping or caking) is problem-free and possible in short cycle times, so that thin-wall components in particular are a possible application.

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These are suitable for producing inscribed moldings of any type, especially for applications as keyboards, monitors and printers.

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Examples

Component A/1

- 5 Polybutylene terephthalate having a viscosity number VN of 130 ml/g and a carboxyl end group content of 34 meq/kg (Ultradur® B 4520 from BASF AG) (VN measured in 0.5% by weight solution of phenol/o-dichlorobenzene, 1:1 mixture at 25°C), comprising 0.65% by weight of pentaerythrityl tetrastearate (component C41 based on 100% by weight of A)

10

Component A/2

PBT as under A/1 with 24% by weight of glass fibers (C42) and 27.5% by weight of a mixture of calcium phosphinate (C43) and melamine cyanurate (C44) in a ratio of 63:37

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Preparation method for polycarbonate C1

General working method:

- 20 In a three-neck flask equipped with stirrer, reflux condenser and internal thermometer, the polyfunctional alcohol was mixed with diethyl carbonate in equimolar amounts according to table 1, and 250 ppm of catalyst (based on the amount of alcohol) were added. The mixture was subsequently heated to 100°C with stirring, and to 140°C in the experiment indicated by *, and stirred at this temperature for 2 h. With increasing
- 25 reaction time, the temperature of the reaction mixture was reduced as a result of the evaporative cooling of the monoalcohol released which sets in. The reflux condenser was then exchanged for a descending cooler, ethanol was distilled off and the temperature of the reaction mixture was increased slowly to 160°C.
- 30 The ethanol which had been distilled off was collected in a cooled round-bottom flask and weighed, and the conversion was thus determined as a percentage compared to the theoretically possible full conversion (see table 1).

- 35 The reaction products were subsequently analyzed by gel permeation chromatography; the eluent was dimethylacetamide; the standard used was polymethyl methacrylate (PMMA).

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	Alcohol	Catalyst	Amount of ethanol distillate based on full conversion [mol%]	Molecular weight M_w M_n	Visc. 23°C [mPas]	OH number [mg KOH/g]
5	TMP+1.2 PO	K ₂ CO ₃	90	1836 1292	7150	455

TMP \triangleq trimethylolpropane

PO \triangleq propylene oxide

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Component B/1

BaSO₄ (Blanc fix)

15

Component B/2

CaCO₃ (black chalk)

Component B/3

20

White barite

Component B/4

25

ZnS/BaSO₄ (lithopone)

Component C31

ZnO

30

Component C32

AgCl

35

Component C33

CuSCN

Processing conditions and test methods

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Extruder:

Conditions for MVR measurement:

Temp.: 260°C

Temp.: 250°C

Residence time: 3 min

Load: 2.16 kg

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Drying conditions: 3 h/80°C/100 mbar

Injection molding machine:

Melt vessel temp.: 260°C

10 Mold temp.: 100°C

Pressure: 13 bar

Predry granules at 70°C over night.

15 Assessment of the laser inscribability (contrast value)

Laser: Nd:YAG, wavelength = 1064 nm

For mode aperture 1.3 mm, inscription rate = 400 mm/sec.

20 Black on white

Table 1

	1	2	3	4	5	6	7	8	1C	9	10	11	12
A/1	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	100	98.0	98.0	98.0	97.5
B/1	0.5				0.5					0.5			
B/2		0.5				0.5					0.5		
B/3			0.5				0.5					0.5	
B/4				0.5				0.5					1
C31	0.5	0.5	0.5	0.5									
C32					0.5	0.5	0.5	0.5					
C33										0.5	0.5	0.5	0.5
C/1	1	1	1	1	1	1	1	1		1	1	1	1
Contrast										1.9			
MVR (cm ³ /10 min)										25.1			

Table 2

	1	2	3	4	5	6	7	8	9	10	11	12
A/3	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	98.0	97.5
B/1	0.5				0.5				0.5			
B/2		0.5				0.5				0.5		
B/3			0.5				0.5				0.5	
B/4				0.5				0.5				1
C31	0.5	0.5	0.5	0.5								
C32					0.5	0.5	0.5	0.5				
C33									0.5	0.5	0.5	0.5
C/1	1	1	1	1	1	1	1	1	1	1	1	1
Contrast	1.5	1.4	1.5	1.4								
MVR (cm ³ /10 min)	16.2	17.8	16.6	16.2	6.95	6.70						

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What is claimed is:

1. A process for inscribing moldings based on thermoplastic polyesters A) or mixtures of these polyesters with up to 70% by weight, based on the total weight of the components, of further additives C), by means of energy-rich radiation,
5 which comprises using, as an additive B) for improving the inscribability, at least one alkali metal carbonate, alkaline earth metal carbonate, alkali metal sulfate or alkaline earth metal sulfate, or mixtures thereof.
- 10 2. The process according to claim 1, wherein use is made additionally of

at least one highly branched or hyperbranched polycarbonate C1) having an OH number of from 1 to 600 mg KOH/g of polycarbonate (to DIN 53240, part 2), or
15 at least one highly branched or hyperbranched polyester C2) of the A_xB_y type where x is at least 1.1 and y is at least 2.1,

or mixtures thereof.
- 20 3. The process according to claims 1 and 2, wherein component C1) has a number-average molecular weight M_n of 100 to 15 000 g/mol.
4. The process according to claims 1 to 3, wherein component C1) has a glass transition temperature T_g of from -80°C to 140°C.
- 25 5. The process according to claims 1 to 4, wherein C1) has a viscosity (mPas) at 23°C (to DIN 53019) of from 50 to 200 000.
6. The process according to claims 1 to 5, wherein an inorganic transition group metal salt is additionally used.
- 30 7. The process according to claims 1 to 6, wherein the source of the energy-rich radiation used is an Nd:YAG laser having a wavelength of 1064 nm which works by the deflection method.
- 35 8. The process according to claims 1 to 7, wherein the source of the energy-rich radiation used is an Nd:YAG laser with frequency doubling with a wavelength of 532 nm.
- 40 9. A thermoplastic molding composition comprising

A) from 10 to 99.9% by weight of at least one thermoplastic polyester,

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- B) from 0.01 to 10% by weight according to claim 1,
- C) from 0.01 to 50% by weight of C1 or C2 or mixtures thereof according to claim 2,
- C3) from 0 to 10% by weight of an inorganic transition group metal salt,
- 5 C4) from 0 to 50% by weight of further additives,

where the sum of the percentages by weight A) to C) always adds up to 100%.

- 10. 10. An inscribed molding, semifinished product or finished product obtainable by the process conditions according to claims 1 to 8 or from the molding compositions according to claim 9.

Process for inscribing moldings

Abstract

- 5 A process for inscribing moldings based on thermoplastic polyesters A) or mixtures of these polyesters with up to 70% by weight, based on the total weight of the components, of further additives C), by means of energy-rich radiation, which comprises using, as an additive B) for improving the inscribability, at least one alkali metal carbonate, alkaline earth metal carbonate, alkali metal sulfate or alkaline earth
- 10 metal sulfate, or mixtures thereof.